# BITTERN MASS BALANCE

# FOR LESLIE SALT CO.

# SAN FRANCISCO BAY AREA FACILITIES

APRIL 1986

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# 1.0 INTRODUCTION

## 1.1 PURPOSE AND SCOPE

The San Francisco Bay Region of the California Regional Water Quality Control Board has requested that Leslie Salt Co. provide a mass balance for bittern at each of our Bay Area facilities -- Newark, Redwood City, and Napa. The balance was to include estimates of bittern generation, evaporation, rainfall, changes in the amount of bittern stored, and losses through leakage.

## 1.2 BACKGROUND

Leslie Salt Co. is attempting to develop markets for and sell as much bittern as possible. As part of that effort, we have been investigating the phase chemistry and mass balance aspects of bittern to assist in developing products. Historical information needed for a balance is for the most part either not available (because it was never measured or kept), or of such a nature as to be not accurate enough or reliable. However, because of the request by the Regional Board, we have attempted to perform a mass balance with the limited information on hand and extrapolation of data when necessary numbers are just not available.

The report which follows describes the following:

- Variables of the mass balance equation necessary to perform a detailed mass balance.
- Information which is either known, can be estimated or which is a guess.
- Approach which was used to prepare the mass balance based on the factors above.
- Results of the above approach.

### 1.2.1 Bittern Systems

Figure 1 is a diagram of the bittern system at each facility. Each plant handles bittern differently, and within a plant bittern has been handled in various ways over the years. The diagram shows the most routine or usual treatment of bittern. At Newark, the bittern is first sent to desalting, and then to the bittern storage ponds. Some of the Newark bittern is sold.

At Redwood City, the bittern is desalted and then sent to storage. None is sold. No desalting occurs at Napa and no bittern is sold.

### 1.2.2 Information Base

Below is an enumeration of the information necessary to do a detailed mass balance along with comments about the information we have on each item.

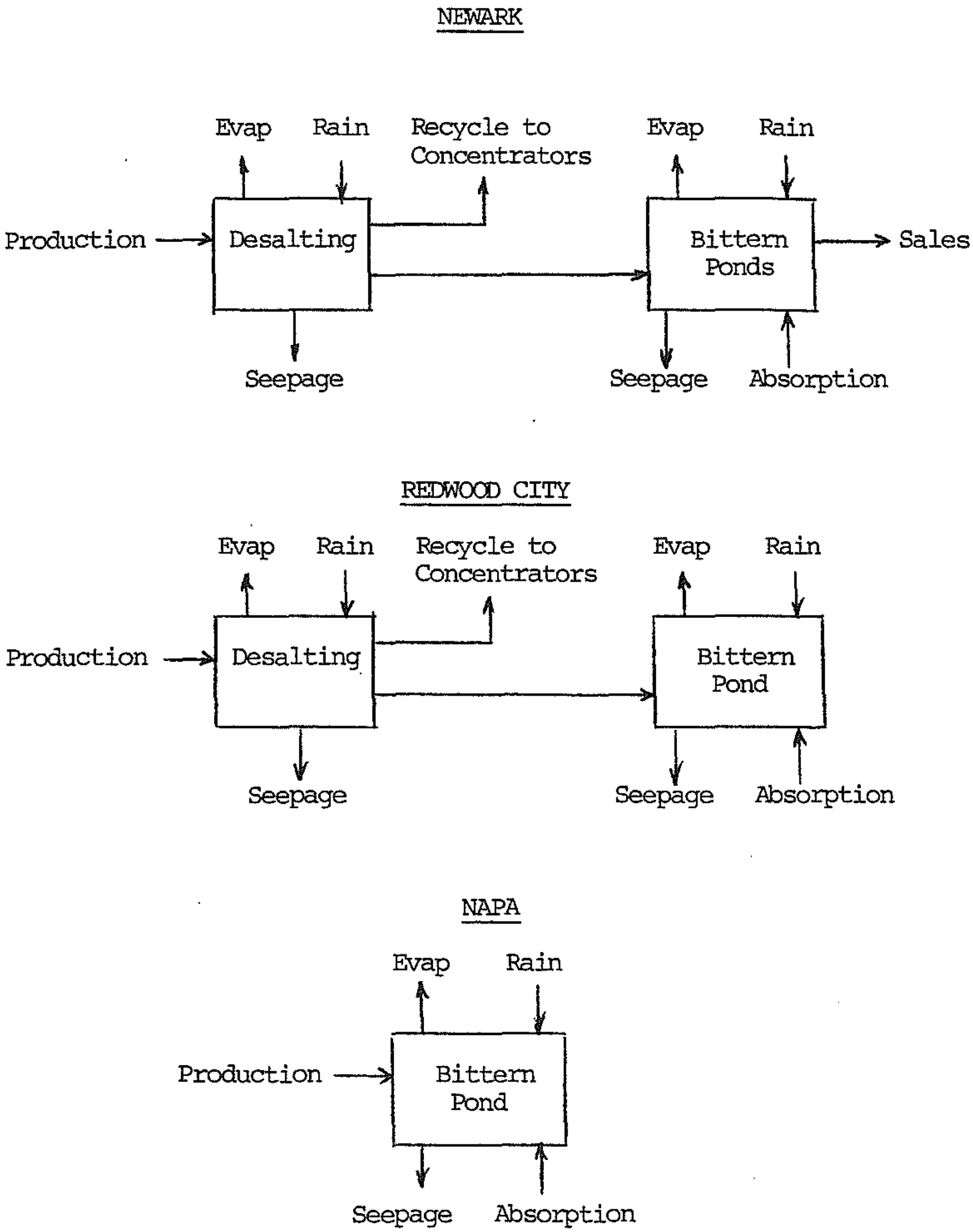

NEWARK
Evap
Rain
Recycle to Concentrators
Evap
Rain
Production
Desalting
Bittern Ponds
Sales
Seepage
Seepage
Absorption
REDWOOD CITY
Evap
Rain
Recycle to Concentrators
Evap
Rain
Production
Desalting
Bittern Pond
Seepage
Seepage
Absorption
NAPA
Evap
Rain
Production
Bittern Pond
Seepage
Absorption

FIGURE 1

1. Amount of bittern removed from crystallizers - This is not measured by any means at Newark and Redwood City, and at Napa is measured by recording pumping hours. In recording pumping hours, the gpm for the pump is assumed from the pump curve and the time of pumping is applied to get the total amount pumped. This method of measurement is used often. However, when using this input in balance calculations for salt, we have found them in the past to be very inaccurate. Quantities measured by this method should not be relied upon for any use.

2. Baume' of virgin bittern - Bittern is removed in batches from the crystallizers beginning usually in July. The watermen target to remove brine to bittern at 31°Be. For various reasons, this cannot always be done. Brine as low as 30°Be and as high as 33°Be has been removed as bittern. The watermen determine °Be to know when to remove the brine to bittern, but the value is not recorded.

3. Seepage - Seepage if any is not measured.

4. Evaporation during desalting - Newark does the most complete desalting. The virgin bittern is moved from the crystallizers to ponds 10 and 11 for desalting where it remains until the end of the summer . At Redwood City, the virgin bittern is desalted in the old bittern pond, but this pond has limited acreage and the desalting is not as complete as at Newark. The bittern is not desalted at Napa. The only evaporation data we have is the actual fresh water evaporation from our standard weather pans. This data has to be adjusted in two ways to apply to bittern. First, an empirical factor (called a pan coefficient) to go from pan conditions to large pond conditions is applied. We have some of these factors which were developed by the government for use on lakes. The second factor is dependent on the concentration of the bittern. As sea water concentrates, the rate of evaporation decreases in relation to fresh water. That relationship is fairly well known through salt making range, but is not known in the bittern concentration range.

5. Amount of solids left behind in desalting - This is not measured. Also the composition of the solids is unknown.

6. Baume after desalting - This is measured sometimes at Newark but is not recorded. It is not known at the other plants.

7. Amount of bittern pumped to bittern ponds - This is measured sometimes at Newark and Napa by pumping hours -- not a reliable number. It is not measured at Redwood City. Composition of the bittern at this point is not known. Bittern movements at Newark between the various bittern ponds is not documented. The °Be is not recorded.

8. Evaporation in bittern ponds - As in #4 above, the only data we have is from our weather station. Correlations in this concentration range are not well known. In fact, the liquid bittern becomes hygroscopic and will absorb moisture from the air. In

our climate, bittern will only concentrate to a point where evaporation equals moisture absorption. At what point this absorption begins, and the relationship with temperature and humidity are not known.

9. Amount and type of bittern solids formed - This information is not known at Redwood City and Napa. We do have sporadic readings at Newark which would measure the amount of buildup of solids. We do not, however, know the bulk density of the solids in order to calculate the amount of solids. We also have little information on the composition of the solids. We know that the solids will change in chemical makeup over time due to dissolving in winter rains, and reforming in different temperature regimes.

10. Rainfall - We know this number fairly accurately from our weather station data.

11. Amount of liquid trapped in the deposited solids - We know there is a significant amount of liquid in the voids in the solids, but have no measure of the amount.

12. Amount shipped - The amounts at Redwood City and Napa are zero. Newark shipments can be determined accurately from our records. Pre-1977 records are questionable.

The table below summarizes our detailed knowledge; items reference item numbers from above:

TABLE 1

| ITEM | KNOW | ESTIMATE | GUESS |
|---|---|---|---|
| 1 | | Nwk, RWC, Napa | |
| 2 | | Nwk, RWC, Napa | |
| 3 | | | Nwk, RWC, Napa |
| 4 | | Nwk, RWC, Napa | |
| 5 | | | Nwk, RWC, Napa |
| 6 | | Nwk | RWC, Napa |
| 7 | | Nwk, Napa | RWC |
| 8 | | Nwk, RWC, Napa | |
| 9 | | | Nwk, RWC, Napa |
| 10 | Nwk, RWC, Napa | | |
| 11 | | | Nwk, RWC, Napa |
| 12 | Nwk | | |

In the case of Newark, of the 12 quantities we would need to know, we could estimate 6, guess at 4, and know 2. At Redwood City of 11 necessary inputs, we know 1 and would have to estimate 4 and guess at 6. At Napa, we need 9 inputs - we know 1, could estimate 4, and guess at 4.

## 2.0 BITTERN MASS BALANCE - APPROACH

Because of the great number of unknowns and guesses needed to perform a detailed mass balance on our bittern systems, it is necessary to use some simplifying assumptions, and then check the effect on the results of varying those assumptions.

We have a lot of data on sea water brines through the salt making stage. However, we have little information on those brines after salt making, in the bittern stage. Much of what we do know about bittern is collected from a variety of sources and is not coordinated or referenced to each other. In 1982, a study was done on bittern starting at the concentration when it was removed from the salt crystallizing beds, to the final concentration that could be achieved given the weather that summer. The data from that study covers most of the bittern range we are interested in, and is the only actual data specific to our situation that is available. Although this study provides one set of data, and does not represent an average of what occurs, it is all we have. This study was used for the following mass balance.

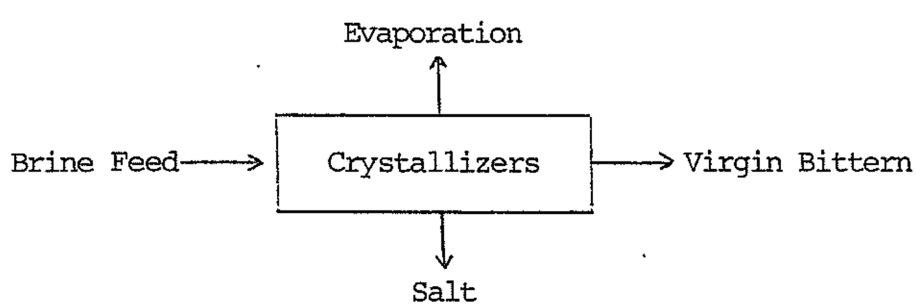
This approach focuses only on the liquid phase of bitterns. It will not follow the solid phase because of a lack of simplifying assumptions that can be made. We will first calculate the amount of virgin bittern generated, and then determine what volume that should shrink to after concentration, and then compare that to what we actually have on hand.

## 3.0 BITTERN MASS BALANCE - CALCULATIONS

### 3.1 Calculated Amount in Storage

Tons of salt produced is the only historical record we have that can be tied to bittern. The first task is to calculate the amount of bittern generated per ton of salt on the stack.

The physical system in the crystallizers is diagrammed below:



The brine feed is saturated at 25.9°Be which we know contains 2.177 pounds of salt per gallon. Virgin bittern is at 31°Be which contains 1.080 pounds of salt per gallon.

To determine how many gallons of virgin bittern output there is per gallon of brine input, we must go to Figure 2. This is a relationship between °Be and volume in the salt making range (origin unknown). This graph has 100% of original volume at 26.15°Be. This, by extrapolation, gives 101.3% at 25.9°Be. At 31°Be the volume percent is 25.5. This ratio of 25.5% to 101.3% says that one gallon of 25.9°Be brine will shrink to 0.25 gallons of 31°Be brine.

Thus the salt entering the crystallizers per gallon of saturated brine is 2.177 pounds, while the salt leaving the crystallizers with 31°Be virgin bittern is (0.25 gal.)(1.080 lb./gal.) = 0.270 lbs. salt. Thus the salt deposited in the crystallizers per gallon of saturated brine is 1.907 pounds by difference.

$$\frac{\text{salt deposited}}{\text{gallon input}} = 1.907 = \frac{\text{salt deposited}}{\text{0.25 gallon output}}$$

$$= \frac{\text{7.63 lbs salt deposited}}{\text{gallon 31°Be bittern}}$$

To make 2000 pounds of salt, we need

$$\frac{\text{2000 pounds}}{\text{7.63 lbs/gal bittern}} = \text{262.1 gallons}$$

Thus one ton of salt on the stack will produce 262.1 gallons of 31°Be bittern. This overstates the amount of bittern produced in that salt loss is experienced during harvesting and washing. The amount of loss is unknown.

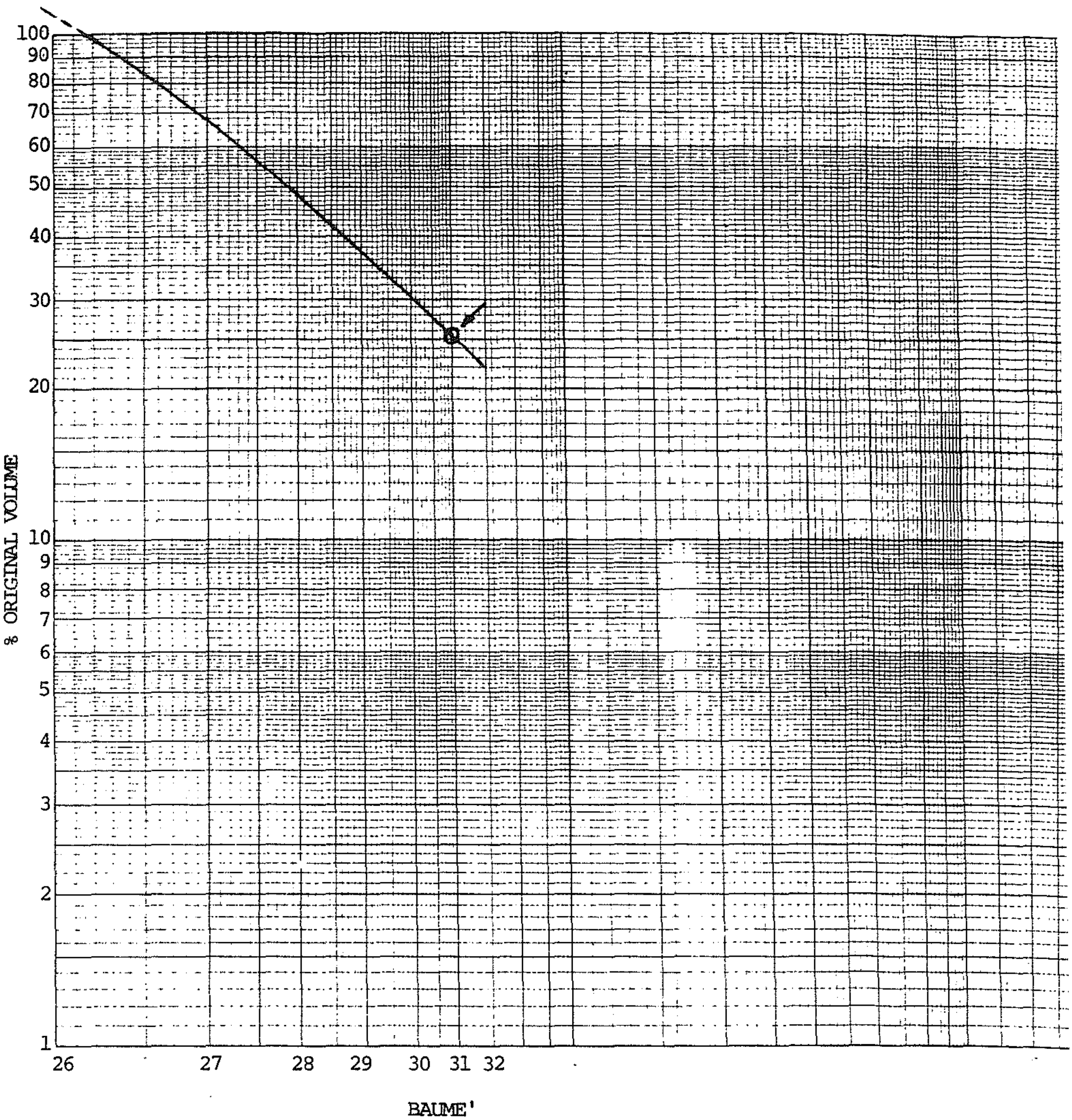
To generalize, we can use the following formula and Figure 2 to determine system output assuming various specific gravities for virgin bittern:

$$\frac{\text{gallons bittern}}{\text{ton salt on stack}} = \frac{\text{(2000) (\% of original vol)}}{\text{2.177 − [(\% of original vol)(lb salt/gal @ °Be)]}}$$

| °Be of Virgin Bittern | % of Original Vol. | Lb. Salt/Gal. | Gal. Bittern / Ton Salt on Stack |
|---|---|---|---|
| 29 | 36 | 1.510 | 440.7 |
| 30 | 30 | 1.295 | 335.5 |
| 31 | 25 | 1.080 | 262.1 |
| 32 | 22 | 0.865 | 221.5 |
| 33 | 19 | 0.650 | 185.0 |

Figure 3 shows this relationship.

FIGURE 2
VOLUME REDUCTION VS. SPECIFIC GRAVITY



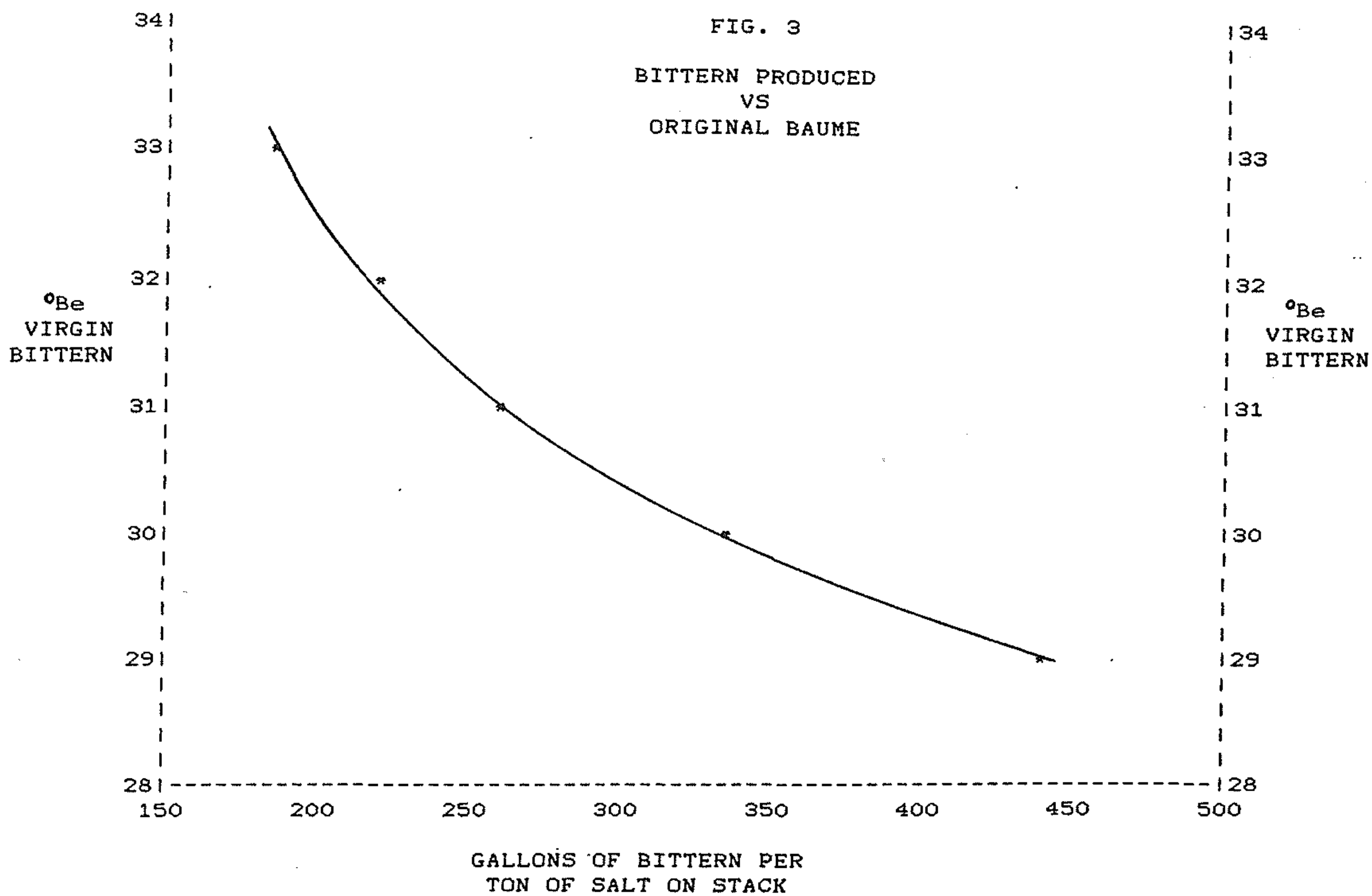


FIG. 3
BITTERN PRODUCED
VS
ORIGINAL BAUME
°Be
VIRGIN
BITTERN
34
33
32
31
30
29
28
150
200
250
300
350
400
450
500
GALLONS OF BITTERN PER
TON OF SALT ON STACK

The second task is to determine at which Baume' we drain bittern from our crystallizers. We do not record this data. We do track pond depth and specific gravity weekly. By inspecting the trends in those two pieces of data, we can infer an approximate average for removing bittern from crystallizers. The average appears to be about 31°Be, but has ranged from 30 to 33.

Our total salt production at Newark since 1971 is 9,478,542 tons. At Redwood City since 1970 we have produced 3,783,596 tons. Since 1965 at Napa we have produced 3,597,319 tons. The dates mentioned above are the years in which Leslie began to store bittern at the specific plant.

Figure 4 gives the relationship between °Be and volume reduction in the bittern range as determined by the 1982 pan study. Since bittern volume varies greatly with specific gravity, and we have bittern at various specific gravities throughout the system, we must calculate all volumes at a reference specific gravity. During the summer, the rainwater from the previous winter is evaporated away and bittern tends to reach an area of relatively constant concentration. The average summer Baume' is about 37.5. This value will be used as an end point concentration for the calculations to follow.

Given the tons of salt produced over the period in question, the point at which bittern is removed from the crystallizers, and the end concentration, the total amount of concentrated bittern produced can be calculated.

Newark

$$\frac{(9{,}478{,}542 \text{ tons salt})(262.1 \text{ gal virgin bittern/ton salt})(0.049 \text{ vol reduction})}{(325{,}900 \text{ gal/acre ft})} = 374 \text{ ac. ft.}$$

Redwood City

$$\frac{(3{,}783{,}596)(262.1)(0.049)}{325{,}900} = 149 \text{ acre feet}$$

Napa

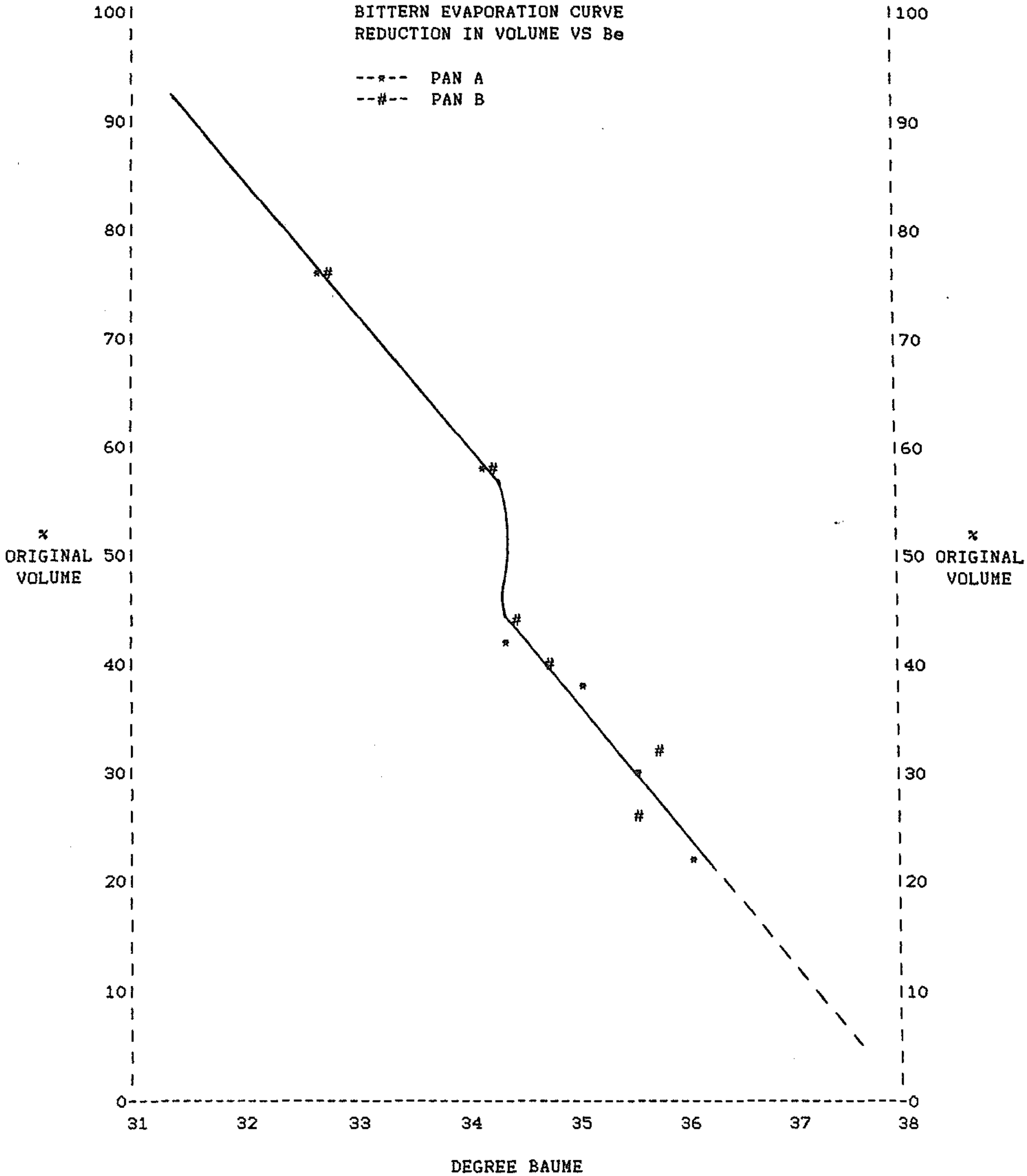
$$\frac{(3{,}597{,}319)(262.1)(0.049)}{325{,}900} = 142 \text{ acre feet}$$

These amounts then are the theoretical volumes of concentrated bittern produced over the years at the three plants given the assumptions made. Since the 1982 bittern pan test stopped at 36°Be, the volume reduction factor is an extrapolation.

## 3.2 Actual Amount in Storage

Bittern is produced each year in batches in late summer. It is desalted (except Napa), then stored. During the winter, rain falls and evaporation continues. Bittern solids are dissolved and

FIG. 4


BITTERN EVAPORATION CURVE
REDUCTION IN VOLUME VS Be
--*-- PAN A
--#-- PAN B
% ORIGINAL VOLUME
% ORIGINAL VOLUME
0
10
20
30
40
50
60
70
80
90
100
31
32
33
34
35
36
37
38
DEGREE BAUME

reformed. Since the bittern phase chemistry is temperature sensitive, different solids are reformed than were originally deposited. Water of hydration and brine entrained between crystals will vary. The following summer the partially concentrated bittern will continue to concentrate -- the endpoint depending on the length and average temperature of that particular summer.

In the past, we have managed our bittern ponds differently. At Newark we began storing bittern in concentrator 10 in 1971. In 1972 bittern storage was moved to pond 13. We began to use pond 12 in 1977 and also began using the small ponds known as FMC 2, 3, 4, 5, and 6 in that year. There were some years that we did not do any desalting. Two years ago we produced no bittern at Newark. Last summer we removed the free liquid from pond 13, brought in bay water to dissolve a solids layer high in salt (from the years we didn't desalt), recrystallized that material for recycle to the concentrators, and replaced the liquids back to pond 13. None of these various operations have been documented as to quantities or analyses. During the December 1983 storm, we did take enough bay water into pond 13 that when the tide receded an unknown amount of bittern was washed into the bay. This has been reported to the Board and is the only such event known at Newark. The pond levee has been topped since that event. Redwood City and Napa have had similar varied histories as to how bittern was handled.

Again, we can make some simplifying assumptions about our system. We will assume that the bittern was desalted and concentrated each year. We will follow the liquid phase only and assume no losses to the Bay.

We know that there is a lot of fluid trapped or entrained in the solids which have deposited on the bottoms of each of the ponds. There is no measure at this time, but we will assume 25% voids in the solids. The following chart calculates the amount of entrained bittern:

TABLE 2

| | POND | POND ACRES | DEPTH OF SOLIDS | ACRE FT. BITTERN | |
|---|---|---|---|---|---|
| NEWARK | 13 | 398.3 | 1.55 Ft. | 149 | |
| | 12 | 246.8 | 0.16 | 10 | |
| | FMC 2,3,4,5,6 | 72.1 | 3.3 | 59 | |
| | FMC Ponds Borrow Ditch | 16.2 | 6.0 | 24 | |
| | 13 Borrow Ditch | 24.1 | 6.0 | 36 | |
| | | | | 278 | Acre Ft. at Newark |
| RWC | 9 | 293 | 0.33 | 24 | Acre Ft. at RWC |
| NAPA | 8 | 130 | 1.2 | 78* | Acre Ft. at Napa |

*Since this pond was recently put into bittern service, the solids are more fluffy. Therefore 50% voids was assumed.

A change in the percent voids assumption will have a direct proportional affect on the results.

We have sold bittern at Newark since we began storing it. We have sales records back to 1977 and have estimated sales prior to that date. Sales prior to 1977 and through 1982 were made almost exclusively to one customer. Therefore sales per year prior to 1977 was assumed to be the average of sales from 1977 to 1982. On this basis, a total of 2043 acre feet have been sold at an average of 34.1°Be. This is equivalent to 109 ac. ft. at 37.5°Be.

An inventory done on 3/5/86 shows that we have 2649.8 ac. ft. of bittern of varying gravities currently on hand at Newark. Using the volume reduction relationships used previously, this computes to 26 ac. ft. at 37.5°Be. Similar measurements were made at Redwood City and Napa.

## 3.3 Results of Mass Balance

We are now ready to compute some totals. We have the bittern theoretically made, the amount sold, the amount trapped in the solids, and the free liquid inventory on hand.

Newark

| | |
|---|---|
| Bittern Made | 374 Ac. Ft. |
| Bittern Sold | - 109 |
| Entrained | - 278 |
| Calc. On Hand | (13) |
| Actual On Hand | 26 |
| Missing or (Extra) | (39) Ac. Ft. |

Redwood City

| | |
|---|---|
| Bittern Made | 149 Ac. Ft. |
| Entrained | - 24 |
| Calc. On Hand | 125 |
| Actual On Hand | 10 |
| Missing or (Extra) | 115 Ac. Ft. |

Napa

| | |
|---|---|
| Bittern Made | 142 Ac. Ft. |
| Entrained | - 78 |
| Calc. On Hand | 64 |
| Actual On Hand | 4 |
| Missing or (Extra) | 60 Ac. Ft. |

## 4.0 SUMMARY AND CONCLUSIONS

The mass balance as calculated in this report used many simplifying assumptions which produce an "order-of-magnitude" result. As explained in detail in earlier sections, much of the necessary data to perform an accurate mass balance simply does not exisit. Therefore assumptions must be made based on either estimates or even guesses. Small yet reasonable changes in these assumptions can dramatically impact the end result. Depending on the assumptions used, the results can show either excess or missing bittern resulting from storage of the material over the years.

Given the information of known but unquantifiable discharges and changes in pond usages, the presented mass balance appears reasonable within an order-of-magnitude.

JP12/28:bep
Attach.
3/31/86

# APPENDIX 1

## ASSUMPTIONS

1. No leakage from the ponds.
2. The volume reduction versus specific gravity relationship derived from the 1982 pan study for bittern concentrations.
3. All bittern is removed from salt crystallizing at 31°Be. This actually varies between 30 and 33°Be.
4. Finished bittern has a specific gravity of 37.5°Be. This actually varies between 36 and 38.5°Be. The 37.5°Be figure is a reasonable average.
5. Bittern has been stored since 1971 at Newark, 1970 at Redwood City, and since 1967 at Napa.
6. Existing data on volume reduction versus specific gravity in the salt making concentrations.
7. Tons of bittern sold since 1977, and estimates of sales before that time.
8. All brine fed to crystallizers is saturated (25.9°Be).
9. Bittern solids eventually contain 25% voids.
10. Liquid bittern entrained in bittern solids is at maximum concentration.
11. Volume reduction on evaporation of rain diluted bittern is the same as that for virgin bittern.

## APPENDIX 2

Although the above results represent the mass balance based on reasonable assumptions, it is important that the sensitivity of the mass balance is also presented herein. The effect on the results by varying some of the assumptions is shown below.

1. If the concentrated bittern is 36°Be instead of 37.5°Be, the amounts missing or (extra) become:

| | | |
|---|---|---|
| Newark | 646 | Acre Feet |
| RWC | 706 | |
| Napa | 649 | |

If, however, concentrated bittern is taken as 37.8°Be, the amounts missing or (extra) would be:

| | | |
|---|---|---|
| Newark | (230) | Acre Feet |
| RWC | 4 | |
| Napa | (50) | |

2. If virgin bittern is removed from the crystallizers at 32°Be and concentrated to 37°Be, the amount of concentrated bittern produced would be:

| | | |
|---|---|---|
| Newark | 587 | Acre Feet |
| RWC | 234 | |
| Napa | 222 | |

These numbers are 4% smaller than the 31°Be case.

If virgin bittern were removed at 30°Be, the amounts would be 14% larger than the 31°Be case.

3. If the volume reduction relationship in the bittern range is incorrect, the final results would be incorrect in proportion to that error.